

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of: **Kanshi CHINONE**

Art Unit: **1793**

Application Number: **10/568,147**

Examiner: **Michael A. MARCHESCHI**

Filed: **February 13, 2006**

Confirmation Number: **7793**

For: **ABRASIVE COMPOUNDS FOR SEMICONDUCTOR PLANARIZATION**

Attorney Docket Number: **062110**

Customer Number: **38834**

DECLARATION UNDER 37 C.F.R. §1.132

Mail Stop Amendment
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Kanshi CHINONE, declare and state that:

1. I majored in Materials Science, Graduate School of Science and Engineering, Ibaraki University, and received a Master of Engineering March, 2000;
2. Since April, 2000 I have been employed at Hitachi Chemical Co., Ltd., and work in the development of CMP slurry in the R&D Group;
3. I am the inventor present application; and
4. I have read and understand the Office Actions to date, including the references cited therein.

Application No.: 10/568,147
Art Unit: 1793

Declaration under 37 C.F.R. §1.132
Attorney Docket No.: 062110

Experimental Term: October 3, 2008 to December 8, 2008

Experimenter: Kanshi CHINONE

Experiments conducted at: 4-13-1, Higashi-cho, Hitachi City, Ibaraki
Hitachi Chemical Co., Ltd., Semiconductor Material Division, Wafer
Process Development Section

(I) Reproduced Experiments of Yoshida Reference

1. Object

The Examiner states that when the polishing slurry described in Yoshida reference (USP No. 6,221,118, the international publication number of the application corresponding thereto: WO098/14987) is compared with the polishing slurry of the invention of the present application, no coarse particles are present in the Yoshida. However, when the slurry in the Yoshida reference is observed by the method described in the specification and claims of the present application, coarse particles are present therein. This matter will be demonstrated hereinafter.

2. Experimental Method

Out of the polishing slurries described in Examples of the present application, a sample appears to have the largest particle diameter was selected while out of Examples of the Yoshida reference, a sample appears to have the smallest particle diameter was selected. Between the two, the contents of coarse particles as well as the numbers of scratches were compared.

3. Preparation of samples

3.1. Sample X

The polishing slurry described in Example 1 of the Yoshida reference was prepared as follows:

Into a container made of aluminum was put 1 kg of cerium carbonate hexahydrate (manufactured by Nippon Yttrium Co., Ltd.; purity: 99.9%), and then the carbonate was fired at 750°C in a box-shaped electric furnace for 2 hours to yield 0.5 kg of cerium oxide. The sample operation was repeated 4 times to yield 2 kg of cerium oxide as a whole.

A jet mill was used to pulverize 2 kg of the prepared cerium oxide.

Into 1000 kg of the resultant pulverized cerium oxide were incorporated 23 g of a 40% solution of ammonium polyacrylate (weight-average molecular weight $M_w = 10,000$) in water (the weight of 23 g corresponded to 12 g of the solid therein) and 8977 g of deionized water, so as to make the total weight into 10 kg. While this mixed liquid was stirred, ultrasonic waves were applied thereto for 15 minutes by use of an ultrasonic cleaner. In this way, a liquid dispersion was produced.

The produced dispersion was filtrated through a filter for mass production (filter fibers were mutually superposed to form pores) having a pore diameter of 1.0 μm , and then deionized water was added thereto so as to adjust the concentration of cerium oxide into 3%. The resultant was used as a sample X.

3.2. Sample Y

The polishing slurry described in Example 1 of the present application was prepared as follows:

Into a container made of aluminum was put 1 kg of cerium carbonate hexahydrate (manufactured by Nippon Yttrium Co., Ltd.; purity: 99.9%), and then the carbonate was fired at 800°C in a box-shaped electric furnace for 2 hours to yield 0.5 kg of cerium oxide. The sample

operation was repeated 4 times to yield 2 kg of cerium oxide as a whole.

A jet mill was used to pulverize 2 kg of the prepared cerium oxide. Thereafter, into 1000 kg of the resultant pulverized product were incorporated 23 g of a 40% solution of ammonium polyacrylate (weight-average molecular weight $M_w = 10,000$) in water (the weight of 23 g corresponded to 12 g of the solid therein) and 8977 g of deionized water, so as to make the total weight into 10 kg. While this mixed liquid was stirred, ultrasonic waves were applied thereto for 15 minutes by use of an ultrasonic cleaner. In this way, a liquid dispersion was produced.

The resultant dispersion was allowed to stand still at room temperature for 20 hours so as to yield a precipitation, and then the supernatant was collected. This supernatant was filtrated through a filter for mass production (filter fibers were mutually superposed to form pores) having a pore diameter of $1.0\ \mu\text{m}$. Thereafter, the liquid was again filtrated through the same filter for mass production, the pore diameter of which was $1.0\ \mu\text{m}$. Deionized water was then added thereto so as to adjust the concentration of cerium oxide into 3%. The resultant was used as a sample Y.

4. Evaluation

4.1. Particle Diameter Measurement

A laser diffraction type particle size distribution meter (trade name: MASTERSIZER MICROPLUS, manufactured by Malvern Instruments Ltd.) was used to measure the D50 (cumulative volume 50% particle diameter) and the content by percentage of particles having sizes of 780 nm or less about each of the samples. The measurement was made under the

following conditions: the refractive index was 1.9285, the light source was a He-Ne laser, and the absorption was zero.

4.2. Large-Particle Content Measurement

The sample X and the sample Y were each diluted 15 times with deionized water, and then 30 g of the sample was filtrated with a filter having a pore diameter of 3 μm (cyclopore track etched membrane filter, manufactured by Whatman Co.). After the filtration, the filter was dried at room temperature, and the weight of the filter was measured. The amount of coarse particles of 3 μm or more size was calculated from an increment in weight over the time from the start of the filtration to the end thereof. Separately, 10 g of the polishing slurry was dried at 150°C for 1 hour, and the solid concentration in the polishing slurry was calculated. From the weight of the coarse particles of 3 μm or more size and the solid concentration, the large-particle content (ppm) was calculated.

4.3. Scratch Number Measurement

Each of the polishing slurries was diluted with deionized water to set the solid concentration therein to 1% by weight. A wafer was then polished therewith by a method described below, and then a surface of the wafer was observed with a microscope to count the number of scratches therein.

[Polish Test Method]

Polish load: 30 kPa

Polish pad: Foamed polyurethane resin (IC-1000), manufactured by Rodel Inc.

Number of rotations: 75 rpm about the polish plate, and 75 rpm about the pad

Polishing slurry supply rate: 200 mL/min

Polish object: P-TEOS film deposited Si wafer (200 mm)

Scratch measuring device:

a) REVIEW STATION manufactured by Olympus Optical Co., Ltd.

(Optical microscope; observing magnification powers: 200 and 1000)

b) SEM Vision G3 manufactured by Applied Materials Inc.

(Electron microscope; observing magnification power: 20000)

5. Results and Consideration

5.1. Results

The evaluation results of the samples X and Y are shown in Table 1.

Table 1: Evaluation Result Comparison

Sample	Filtration method in [3. Preparation of Samples]	Particle diameter measurement		Large-particle content (3.0 μm or more)	The number of scratches		
		D50	Content of particles 780 nm or less in particle diameter		200	1000	20000
X	A	200 nm	0%	820 ppm	0	47	212
Y	B	200 nm	0%	450 ppm	0	22	34

The reference symbols concerning the filtration method mean the following:

A: Sample was filtrated through a filter having a pore diameter of 1.0 μm

B: Sample was filtrated through a filter having a pore diameter of 1.0 μm , and again filtrated through the same filter, the pore diameter of which was 1.0 μm

5.2. Consideration

The samples X and Y were filtrated through the same filter. However, the large-particle content in the sample X was smaller than that in the sample Y. This appears to be because about any commercially available filter, the particle capturing rate that particles having particle diameters equal to or larger than its nominal particle diameter are captured may not be 100%. About any commercially available filter, filter fibers may be damaged or deformed so that the sizes of the pores therein are varied. As a result, particles may easily pass through the filter. In a case where the shape of particles is slender, the particles may not be easily captured in accordance with the direction of the particles when the particles pass through the filter medium. For these reasons, in general, about any commercially available filter, the particle capturing rate that particles having particle diameters equal to or larger than its nominal particle diameter are captured is not 100%. About the sample Y, the same filter as about the sample X was used; however, when the filtration was repeated, the particles once passed through the filter were captured so that the large-particle content was decreased. It appears that the decrease also results in a decrease in the number of the scratches.

The number of the scratches according to the sample X and that according to the sample Y were each measured while the observing magnification power was varied. As a result, no scratch was observed with an observing magnification power of 2000 according to each of the samples. In a case where the power was 1000, the number according to the sample X > that according to the sample Y. In a case where the power was 20000, the number according to the sample X >> that according to the sample Y. As the observing magnification power was higher,

the number of scratches was increased according to each of the samples and the difference between the number of scratches according to the sample X and that according to the sample Y became larger. The observation with the electron microscope demonstrated that most of the scratches had a size of about 1 μm . A photograph of typical examples of the scratches is shown in Fig. 1. From this matter, it has been proved that when the large-particle content is decreased, scratches having a size of 1 μm or less, which are not easily detected with any optical microscope, are decreased. Fig. 1 (attached) is a photograph showing typical examples of the scratches.

6. Conclusion

From the comparison results between the polishing slurry sample X produced in accordance with the technique described in Yoshida reference (USP No. 6,221,118/WO 098/14987) and the inventive polishing slurry sample Y described in the specification of the present application, it was found that in the sample X, coarse particles, which are not detectable with a particle size distribution meter and should be in a fine amount, are contained in a large amount. Thus, the cerium oxide particles of Yoshida reference do not meet the particle size diameters as claimed. Further the number of given scratches is large. As the number of the scratches is larger and the size thereof is larger, the yield of semiconductor devices is made lower. It has been verified that in order to decrease such scratches, it is effective to use, as an index, the content of coarse particles having a particle diameter of 3 μm or more, which is described in the specification of the present application, and reduce this content.

(II) Reproduced Experiments of the Pasqualoni reference

1. Object

It is demonstrated that the invention described in Pasqualoni reference (US2003/0064671) cannot be applied to any polishing slurry where cerium oxide (ceria) particles are used as polishing particles as in the present invention.

More specifically, the following is demonstrated: about the polishing slurry wherein cerium oxide particles are used as polishing particles, a direct correlation does not exist between the condition described in the Pasqualoni (the number of particles having a particle diameter of 0.5 μm or more is 150,000 or less in 30 μL of a polishing slurry), which will be referred to as Pasqualoni's condition hereinafter, and the advantageous effect of yielding a good polish speed (polishing rate) while restraining the generation of scratches.

Additionally, about the polishing slurry wherein cerium oxide particles are used as polishing particles, the condition that the content of particles having a particle diameter of 3 μm or more is 500 ppm in the solid, which will be referred to as the present invention condition hereinafter, has a correlative relationship with the advantageous effect of yielding a good polish speed while restraining the generation of scratches.

2. Experimental Method

Various samples as described below were prepared, and the particle contents therein and the polish speeds thereof were examined.

Sample A: Sample wherein silica particles were used as abrasive particles to satisfy Pasqualoni's condition, the sample corresponding to Example 1 of Pasqualoni reference

Sample B: Sample wherein cerium oxide particles were used as abrasive particles to satisfy Pasqualoni's condition

Sample C: Sample wherein cerium oxide particles were used as abrasive particles not to satisfy Pasqualoni's condition but to satisfy the present invention condition

Sample D: Sample wherein cerium oxide particles were used as abrasive particles not to satisfy Pasqualoni's condition but to satisfy the present invention condition provided that the number of particles of 3 μm or more particle diameter was larger than that in the sample C under the present invention condition

Sample E: a sample wherein cerium oxide particles were used as abrasive particles neither to satisfy Pasqualoni's condition nor the present invention conditions

3. Preparation of Samples

3.1. Sample A

To 91.83 g of deionized water were added 8 g of a commercially available fumed silica (available from Wako Pure Chemical Industries, Ltd., particle diameter: 70 nm), 0.05 g of a hydrogen peroxide water (available from Wako Pure Chemical Industries, Ltd., concentration: 30%), 0.01 g of benzotriazole (available from Wako Pure Chemical Industries, Ltd.), and 0.11 g of an ammonia water (available from Wako Pure Chemical Industries, Ltd., concentration: 28%) (the weight of 0.11 g corresponded to 0.03 g of the solid therein), and then the components were quietly stirred to produce a polishing slurry. This polishing slurry was filtrated through a filter having a pore diameter of 0.5 μm (DISMIC series, manufactured by Advantech Co., Ltd.). The resultant sample was used as the sample A.

3.2. Sample B

To 55.56 g of deionized water was added 44.44 g of a commercially available cerium oxide (available from Wako Pure Chemical Industries, Ltd., particle diameter: 22 to 44 nm, concentration: 18%), and then the components were stirred. An ultrasonic cleaner was used to apply ultrasonic waves thereto for 15 minutes to produce a liquid dispersion. This dispersion was filtrated through a filter having a pore diameter of 0.5 μm (DISMIC series, manufactured by Advantech Co., Ltd.). The resultant sample was used as the sample B.

3.3. Sample C

Into a container made of aluminum was put 1 kg of cerium carbonate hexahydrate (manufactured by Nippon Yttrium Co., Ltd., purity: 99.9%), and then the carbonate was fired at 800°C in a box-shaped electric furnace for 2 hours to yield 0.5 kg of cerium oxide. The sample operation was repeated 4 times to yield 2 kg of cerium oxide as a whole.

A jet mill was used to pulverize 2 kg of the prepared cerium oxide. Into 1000 kg of the resultant pulverized cerium oxide were incorporated 23 g of a 40% solution of ammonium polyacrylate (weight-average molecular weight $M_w = 10,000$) in water (the weight of 23 g corresponded to 12 g of the solid therein) and 8977 g of deionized water, so as to make the total weight into 10 kg. While this mixed liquid was stirred, ultrasonic waves were applied thereto for 15 minutes by use of an ultrasonic cleaner. In this way, a liquid dispersion was produced. The resultant dispersion was allowed to stand still at room temperature for 20 hours to yield a precipitation, and then the supernatant was collected. This supernatant was filtrated through a filter having a pore diameter of 0.5 μm (DISMIC series, manufactured by Advantech Co., Ltd.).

The resultant sample was used as the sample C.

3.4. Sample D

In the same manner as in the item 2.3, 10 kg of a liquid dispersion was produced, and then the dispersion was allowed to stand still at room temperature for 20 hours to yield a precipitation. The resultant supernatant was collected. This supernatant was filtrated through a filter for mass production (filter fibers were mutually superposed to form pores) having a pore diameter of 1.0 μm . Thereafter, the liquid was again filtrated through the same filter for mass production, the pore diameter of which was 1.0 μm . Deionized water was then added thereto so as to adjust the concentration of cerium oxide into 3%. The resultant was used as the sample D.

3.5 Sample E

In the same manner as in the item 2.3, 10 kg of a liquid dispersion was produced, and then the dispersion was allowed to stand still at room temperature for 20 hours to yield a precipitation. The resultant supernatant was collected. Without filtrating the supernatant, deionized water was then added thereto so as to adjust the concentration of cerium oxide into 3%. The resultant was used as the sample E.

4. Evaluation

4.1. Particle Diameter Measurement

The dynamic light scattering particle size distribution (with a device (LB-500) manufactured by Horiba Ltd.) and the D50 (cumulative volume 50% particle diameter) were measured. The measurement about the sample A was made under the following conditions: the sample refractive index was 1.450 and the dispersing medium refractive index was 1.333. The

measurements about the samples B to E were made under the following conditions: the sample refractive index was 2.1 and the dispersing medium refractive index was 1.333.

4.2. Solid Concentration Measurement

Before and after the filtration, 10 g of each of the polishing slurries was dried at 150°C for 1 hour, respectively, so as to calculate the solid concentrations in the polishing slurry, respectively.

4.3. Large-Particle Number Measurement (measurement about Pasqualoni's condition)

A large-particle measuring device (ACCUSIZER 780A, manufactured by Particle Sizing Systems Co.) was used to measure the number of large particles having a particle diameter of 0.5 μm or more. One milliliter of each of the samples was used, and diluted 3 times in the measuring device to prepare a measuring liquid, and then the number of the large particles in 1 mL of the measuring liquid (corresponding to 30 μm of the sample) was measured.

4.4. Large-Particle Content Measurement (measurement about the present invention condition)

The polishing slurries were each diluted 15 times with deionized water, and then 30 g of the sample was filtrated with a filter having a pore diameter of 3 μm (cyclopore track etched membrane filter, manufactured by Whatman Co.). After the filtration, the filter was dried at room temperature, and the weight of the filter was measured. The amount of coarse particles of 3 μm or more size was calculated from an increment in weight from the start of the filtration to the end thereof. Separately, 10 g of the polishing slurry was dried at 150°C for 1 hour, and the solid concentration in the polishing slurry was calculated. From the weight of the coarse particles of 3 μm or more size and the solid concentration, the large-particle content was

calculated.

4.5. Polish speed

Each of the polishing slurries was used to polish a film-deposited wafer by a method described below. The thickness of the wafer was measured before and after the polishing. From the difference therebetween, the polish speed was calculated. Moreover, an electron microscope was used to count the number of scratches therein.

[Polish Test Method]

Polish load: 30 kPa

Polish period: 1 minute

Polish pad: Foamed polyurethane resin (IC-1000), manufactured by Rodel Inc.

Number of rotations: 75 rpm about the polish plate, and 75 rpm about the pad

Polishing slurry supply rate: 200 mL/min

Polish object: P-TEOS film deposited Si wafer (200 mm)

Light scattering film-thickness measuring meter: NANOSPEC AFT-5100 manufactured by Nanometrics Inc.

Scratch measuring device: SEM VISION G3 manufactured by Applied Materials Inc.

(Electron microscope; observing magnification power: 20000)

5. Results and Consideration

The evaluation results of the samples A to E are shown in Tables 1 and 2.

Table 1: Evaluation Result Comparison

Sample	Filtration diameter in 3.Preparation of Samples	Solid concentration		Particle diameter D50	Pasqualoni's conditions	Present invention condition
		Before filtration	After filtration			
A	0.5 μm	8%	8%	68 nm	89000	6 ppm
B	0.5 μm	8%	8%	47 nm	110000	6 ppm
C	0.5 μm	10%	0.2%	78 nm	330000	27 ppm
D	1.0 μm (*)	3%	3%	220 nm	> 1000000	450 ppm
E	none	3%	3%	220 nm	> 1000000	950 ppm

(*): The sample was filtrated through a filter having a pore diameter of 1.0 μm , and again filtrated through the same filter, which had the pore diameter of 1.0 μm .

Table 2: Polishing Result Comparison

Sample	Polish speed	The number of scratches
A	120 nm/min	4
B	50 nm/min	5
C	40 nm/min	8
D	620 nm/min	34
E	620 nm/min	230

About the sample A, it was confirmed that the results described in Pasqualoni reference were reproduced concerning both of the large-particle number and the polish speed and further the large-particle content was also low.

On the other hand, about the sample B, the number of the large particles in a volume of 30 μL fell into the scope defined in the reference, but the polish speed was lower than that of the sample A.

About the sample C, the solid concentration was largely lowered after the filtration, and the number of the large particles in a volume of 30 μL did not fall into the scope defined in the reference. The polish speed was lower than that of the sample A.

About the sample D, the solid concentration did not lower over the time from the start of the filtration to the end thereof as compared with the sample E. Thus, it appears that only a very small amount of the large particles was selectively removed so that an improvement in the polish speed was consistent with the prevention of polish scratches.

From the above-mentioned results, it has been understood that about the polishing slurry using cerium oxide particles as abrasive particles, the polish speed is remarkably lowered when the number of particles having a particle diameter of 0.5 μm or more is decreased to 150000 or less per 30 μL . In other words, in the case of using small particles beforehand or removing particles having a particle diameter of 0.5 μm or more by filtration, the number of particles having a particle diameter effective for polishing is small so that the polish speed is reduced.

Accordingly, by the use of the polishing slurry using cerium oxide particles as abrasive particles as in the present invention, it is effective for making unexpected improvements in the polish speed consistent with the prevention of polish scratches not to decrease the number of particles 0.5 μm or more in particle diameter but to decrease that of particles 3 μm or more in particle diameter.

6. Conclusion

According to the above, the invention described in Pasqualoni reference (US2003/0064671) can be applied to a case where silica or alumina particles are used as abrasive particles; however, Pasqualoni's invention cannot be applied, as it is, to any polishing slurry where cerium oxide particles are used as abrasive particles since cerium oxide particles exhibit a behavior different from those of other particles.

Application No.: 10/568,147
Art Unit: 1793

Declaration under 37 C.F.R. §1.132
Attorney Docket No.: 062110

I declare further that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Further Declarant saith not.

Kanshi Chinone
Name: Kanshi CHINONE

Date: April 6, 2009

Fig. 1: Photograph of typical examples of the scratches

